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Abstract. In modern fruit supply chain a common method to trigger ripening is to keep fruits inside special chambers and initiate the ripening process through administration of ethylene. Ethylene is usually administered through cylinders with inadequate control of its final concentration in the chamber. The aim of this study is the development of a new technology to accurately regulate ethylene concentration in the atmosphere where fruits are preserved: a polymeric film, containing an inclusion complex of α-cyclodextrin with ethylene, was developed. The complex was prepared by molecular encapsulation which allows the entrapment of ethylene into the cavity of α-cyclodextrin. After encapsulation, ethylene can be gradually released from the inclusion complex and its release rate can be regulated by temperature and humidity. The inclusion complex was dispersed into a thin polymeric film produced by UV-curing. This method was used because is solvent-free and involves low operating temperature; both conditions are necessary to prevent rapid release of ethylene from the film. The polymeric films were characterized with respect to thermal behaviour, crystalline structure and kinetics of ethylene release, showing that can effectively control the release of ethylene within confined volume.

INTRODUCTION

In modern fruit supply chains products are often wasted in the path between the harvest and the final user consumption because of lack of control over the ripening process. The harvest of unripen fruits, and the initiation of the ripening process just before its delivery to the final consumer, was found to reduce the waste of fruits.

Ripening process involves many biological and physiological changes in the fruits, as such changes in carbohydrate composition, changes in colour and texture, formation of aroma and flavour[1]. All these characteristics are dependent on the stage of ripening and influence consumer acceptability. Fruits can be distinguished on the basis of the ripening mechanisms in climacteric and non-climacteric fruits. Fruits that have a climacteric behaviour show a dramatic increase in respiration rate and ethylene production during the ripening process and can still ripen after harvest[2]. In addition, the ripening of climacteric fruits is regulated by many natural growth regulators (ethylene, auxins, cytokinins, gibberellins and abscisic acid). On the other hand, non-climacteric fruits do not show a rapid ripening phase and do not ripen after harvest[2,3].

In case of climacteric behaviour, it is possible to control ripening by controlling respiration rate and modifying the atmosphere where the fruits are stored. In particular, ethylene plays an important role as it initiates the ripening process, and it can be considered a catalyst for the process itself. Ethylene is synthesized by all types of plant and starts its biological activity at very low concentration, in a range from few units to hundreds of ppm[3,4,5].

Controlled ripening process is currently carried out in insulated chambers with modified and controlled atmosphere. In particular, ripening chambers are designed in order to control temperature, moisture and ethylene concentration. The control of ethylene concentration in the ripening room is challenging, as it is mostly administrated from cylinders and injected periodically. In addition to safety issues (as ethylene is a flammable and explosive gas) it is very difficult to ensure a correct concentration into the room. Commonly, the ethylene excess results in accelerated rates of ripening and in a production of overripened fruits.

In this work a new technology has been developed in order to achieve a more precise regulation of the ethylene concentration in the ripening chambers. In particular, a thin film of PEGDA with embedded ethylene/α-cyclodextrin inclusion complex has been used to study the ethylene release kinetics at different temperature and humidity conditions.

Ethylene/α-cyclodextrin inclusion complex (IC) has been prepared by molecular encapsulation which allows the entrapment of a guest compound (ethylene) into the cavity of α-cyclodextrin (α-CD)[6]. At certain conditions of temperature and relative humidity, the guest compound will leave the cavity of the host compound according to a certain kinetics[7,8]. Thus, the IC can be used in a confined chamber in order to control the ripening process. Furthermore, the IC has been dispersed in a polymeric matrix in order to produce a smart packaging. In this work UV-curing technique has been used to obtain crosslinked films, since it allows the production of cured polymer films in short time and without use of neither solvents or high temperature as they could promote premature ethylene release[9,10]. UV curing process is based on a photochemical reaction and consists in the irradiation with UV rays of a solution made of a monomer/oligomer resin and a photo-initiator compound. The photo-initiator compound absorbs UV energy and produces the first active species of the reacting chain. As heat generated is only connected to the exothermal crosslinking reaction, the temperature increase during the curing process can be considered negligible. Furthermore, the absence of solvents, the lowest energy consumption and the use of biocompatible oligomers and photo-initiators make this technique sustainable and environmental friendly[9].

EXPERIMENTAL SECTION

Materials and methods

IC crystals were produced via molecular encapsulation from α-cyclodestrin (Cavamax W6 Food, 98% purity, Wacker-Chemie, Munich, Germany) and ethylene (99,9% purity, Siad, Bergamo, Italy). Poly (ethylene glycol) diacrylte PEGDA resin of average Mn 700 (Sigma Aldrich, Milano, Italy) and the photoinitiator 2-hydroxy-2-methyl-1-phenyl-propan-1-one Darocur® 1173 (BASF, Cesano Maderno, Italy) were used to produce thin films with embedded IC.

Production of Ethylene/α-CD inclusion complex

The molecular encapsulation process for the IC production was performed in a 500-ml high-pressure reactor (LimboLi, BuchiGlasUster, Uster, Switzerland). In Fig.1 a schematic of the plant for the production of the inclusion complex is shown. A saturated water solution of α-cyclodextrin (α-CD) was placed in the reactor and exposed to a high partial pressure of ethylene to increase the solubility of the gas in the aqueous phase. Since the solubility of the IC in water is much lower than the solubility of raw α-CD, the IC precipitates from the solution and crystal are easily collected using a paper filter, after depressurization of the reactor. The IC were dried at room temperature until they reached constant weight. The effect of process conditions on yield was studied varying ethylene partial pressure and the residence time in the reactor.

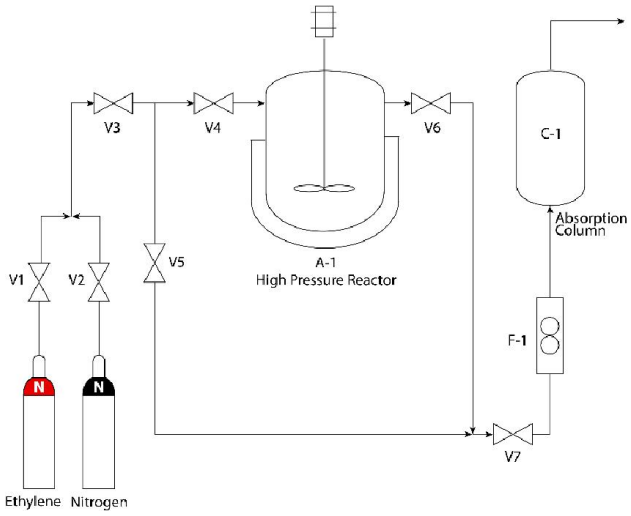


FIGURE 1. Schematic of the plant for inclusion of ethylene into α-CDs.

Production of PEGDA films filled with IC

The films were prepared using a photoinduced curing of a diacrylated resin: Poly (ethylenglycol) Diacrylate (PEGDA). IC crystals, and in some cases raw α-CD powder, were dispersed into the resin before exposure to UV lamp (Hg Medium Pressure, Helios Italquartz, Milano, Italy). UV-curing was performed in inert atmosphere, to avoid oxygen quench, for 30 seconds of irradiation time.

Thermal and structural characterization

The IC crystals and raw α-CD powder were characterized by different thermal analyses in order to point out any differences. Differential scanning calorimetry (DSC Q200, TA Instrument, New Castle, USA) analyses were performed with a temperature ramp of 5 °C/min within a range of -80 and 250 °C. Thermogravimetric analyses (TGA STDA851^e, Mettler Toledo, Columbus, Switzerland) were performed from room temperature to 300 °C. X-rays diffractometry (Pananalytical X'Pert MRD PRO, Almelo, Netherland) using Cu Kα radiation with Ni beta filter, were performed in a wide range of angles, from 5° to 70°.

Infrared spectroscopy FT-IR analyses (Nicolet 5700, Thermo Scientific, Waltham, USA) cooled through liquid nitrogen were carried out to study the conversion rate of the PEGDA films curing process.

Ethylene release tests

Release tests of ethylene from the complex inclusion were performed under controlled conditions. IC samples were placed in the measurement cell of a water activity measurer (LabMaster-aw, Novasina, Lachen, Switzerland) to keep temperature and relative humidity (RH) at fixed values. Two values of temperature (30 and 50 °C) and two values of RH (73% and 97%) were studied. IC samples were extracted from the cell at regular time intervals and analyzed in the following way: they were dissolved in distilled water into a gastight vial, where ethylene was instantly released and accumulated in the vial headspace. A known volume of gas was withdrawn from the vial headspace using a gastight syringe and analyzed via a gas chromatograph (Agilent 6890 Plus GC, Hewlett-Packard, Palo Alto, USA) equipped with capillary column (HP-5 Cross-Linked 5% phenyl methyl siloxane, Hewlett-Packard, Palo Alto, USA) and a flame ionizing detector (FID).

Release of ethylene from the polymeric films containing IC crystals were carried out as well. In this study, the release tests were performed at ambient temperature (25 °C) in saturation (100% RH) and quasi-saturation (97% RH) conditions. During the tests in saturated atmosphere, the film samples were suspended above a liquid water layer in a gastight vial and a given volume of the headspace gas was daily drawn and analyzed by GC. In the case of non-saturated atmosphere, the films were placed into the cell of the water activity measurer, adopting the same procedure of the IC crystal release tests. The film samples were taken at fixed time intervals and immersed into liquid water stored in gastight to obtain, in few days, the complete release of the ethylene.

The kinetics of ethylene released from both IC crystals and PEGDA films was described by Avrami model[11]. The model is characterized by two parameters, which Ho *et al*.[8] related to the release kinetics and the release mechanism. However, in this study the Avrami's model was used as a fitting tool to describe experimental data.

RESULTS AND DISCUSSION

Effect of exposure time and ethylene overpressure on precipitation yield

Ethylene pressure and exposure time affect the IC yield as shown in Fig.2. An increase of ethylene partial pressure inside the reactor resulted in an increased yield since it enabled more ethylene to dissolve in the solution, thus granting a higher rate of reagent supply into the reacting volume. An increase in time of ethylene exposure resulted in an increased yield since the process required many days to reach equilibrium. However, after one hundred hours at 10 MPa of ethylene, the yield seemed to be time-independent. Probably, the reaction equilibrium was reached or no more IC crystals were able to precipitate since it was impossible to reach the saturation within the solution.

The tests on the maximum ethylene concentration inside the IC showed a constant value regardless of the complexation process parameters. This value was around 1 mol of ethylene per mole of IC and can be considered independent of process parameters.

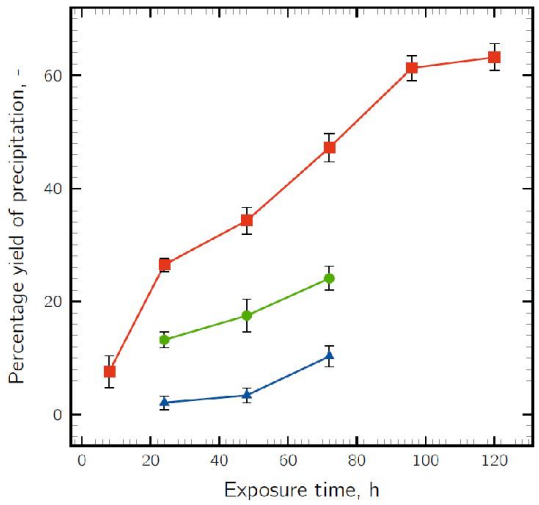


FIGURE 2. Effects and exposure time on the molecular encapsulation yields of ethylene overpressure ([▲] 0.2 MPa, [●] 0.5 MPa and [■] 1.0 MPa).

Characterization of Ethylene/α-CD inclusion complex

Thermal analyses (Fig.3) highlighted a different behaviour between raw α-CD and the IC, and even between IC crystals obtained in different process conditions. DSC showed the presence of multiple and different crystalline structures in α-CD and IC with different melting temperatures. In addition, the melting temperatures in the IC samples were generally lower compared to those of α-CD.

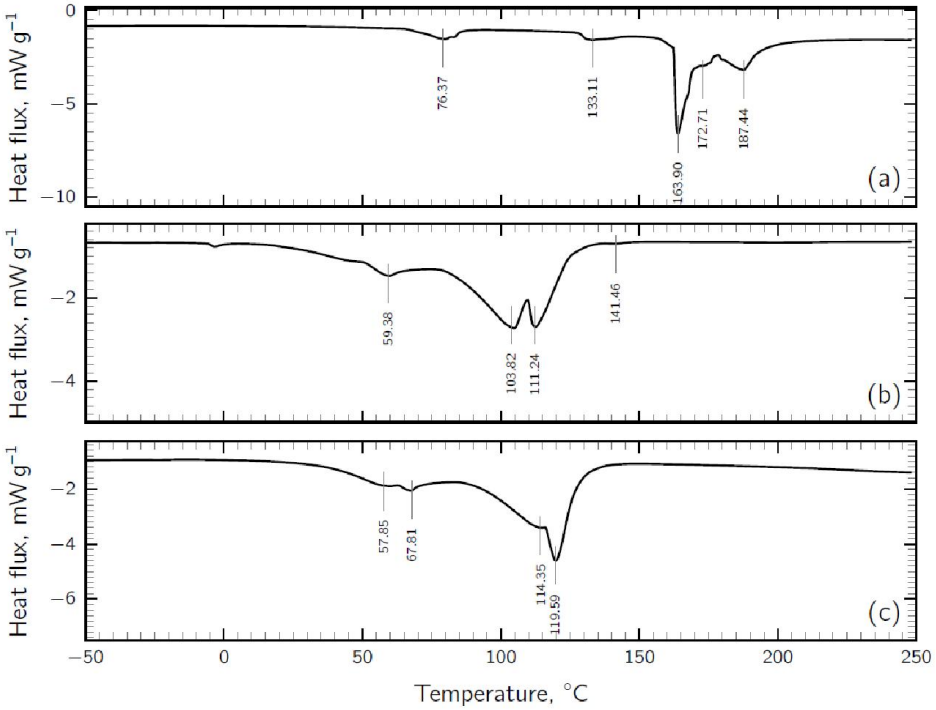


FIGURE 3. DSC scans of (a) α-CD, (b) IC produced at 1.0 MPa in 72 h and (c) IC produced at 1.0 MPa in 96 h.

TGA analyses showed differences in the release of volatile compounds from α-CD and IC crystals. The α-CD had two steps of weight loss while the IC had three steps. This may be due water adsorbed to the IC crystals with different

energy levels. It can be excluded that one of the IC weight loss step is due to ethylene release from the samples since ethylene in released continuously during the analysis and the total ethylene amount was very small.

As shown in Fig.4, XRD diffractograms of (a) α-CD and (b) IC were different, as the IC structure, in fact, depends essentially on the type of molecule complexed in the cyclodextrin cavity. XRD spectra also showed slight differences even between samples of IC produced using different process conditions, suggesting the presence of different polymorphs.

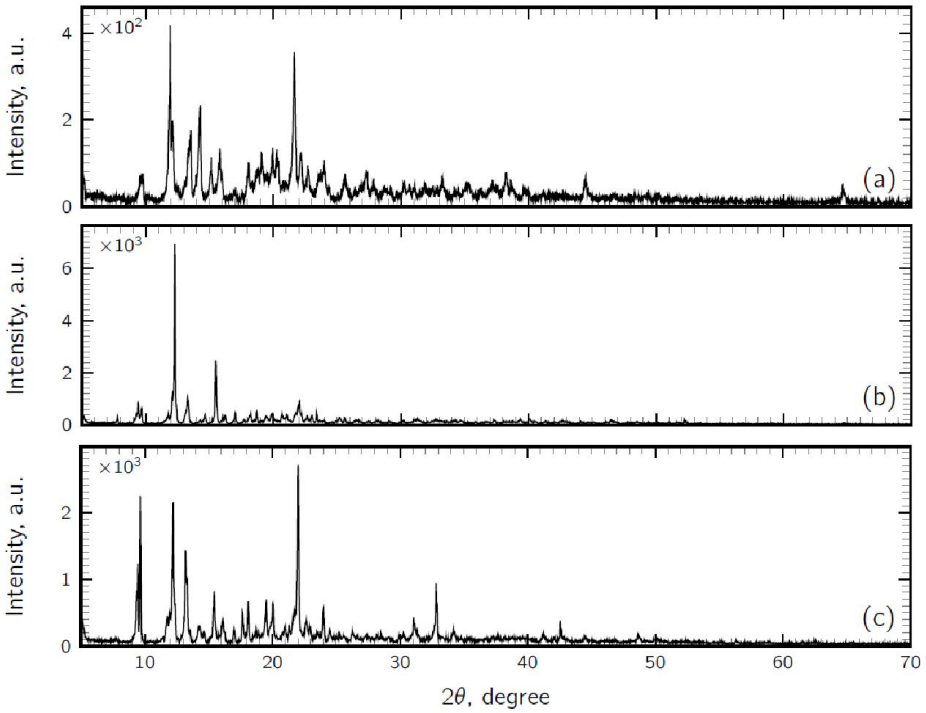


FIGURE 4. XRD scans of (a) α-CD, (b) IC produced at 0.5 MPa in 72 h ad (c) IC produced at 1.0 MPa in 72 h.

Characterization of PEGDA UV-cured films

IR spectra showed that UV-curing conversion of PEGDA was the same in the case of α-CD loaded and plain films. The addition of the filler, thus, did not modify the polymerization process. In case of films with IC crystals the conversion rate could not be measured from IR spectra because of the interference between reactive (α-CD) and non-reactive (ethylene) carbon-carbon double bonds. DSC analyses of the films with embedded IC showed that the crystals did not alter the PEGDA glass transition temperature (T_g) value. Since the T_g is linked with crosslinking density, this results indicated that the crystals had no effects on the curing conversion.

Ethylene release kinetics

As shown in Fig.5 and Fig.6, ethylene release from the crystals showed a kinetics dependent on temperature and humidity. As reported in Fig.5 (a), temperature increase resulted in an increased release rate of ethylene from the inclusion complex: after 120 hours, the ethylene released at 50°C was about 50%, whereas it was under 40% in case of IC at 30°C. In Fig.5 (b) the release curves at 30°C and for relative humidity respectively of 73% and 97% are shown. The release is highly affected by humidity: 20% decrease in relative humidity resulted in a decrease of ethylene release rate of about 50%.

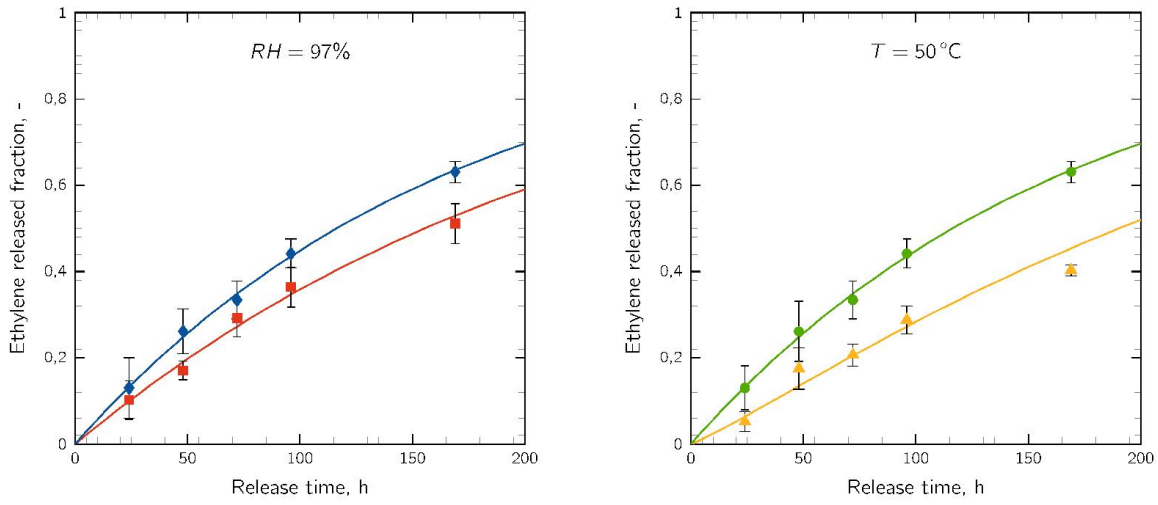


FIGURE 5. Ethylene release curves as obtained using different conditions. (a) Ethylene release at 97% UR at (■) 30 °C and (♦) 50 °C. (b) Ethylene release at 50 °C and at an UR of (▲) 73% and (●) 97%.

The ethylene release kinetics from PEGDA polymeric films was also studied. As shown in Fig.6, although one should speculate that the polymeric matrix offers greater mass transfer resistance to ethylene, the ethylene released from PEGDA was unexpectedly faster than that from the IC alone. The high gas diffusion into the polymer film cannot explain alone such a fast release kinetics. In fact, as the time for ethylene complete release from IC is estimated be about 1000 hours, the release from PEGDA was completed in less than 250 hours. It is hypothesized that this high diffusivity of ethylene in the polymeric film might be promoted by the very low T_g value of the film at room temperature and the hygroscopic characteristics of PEGDA. Water condensed on the polymer surface and penetrated into the matrix, not only promoted the plasticization of the film (and the increase of diffusive coefficient), but also extracted ethylene from the crystals dispersed into the polymer film.

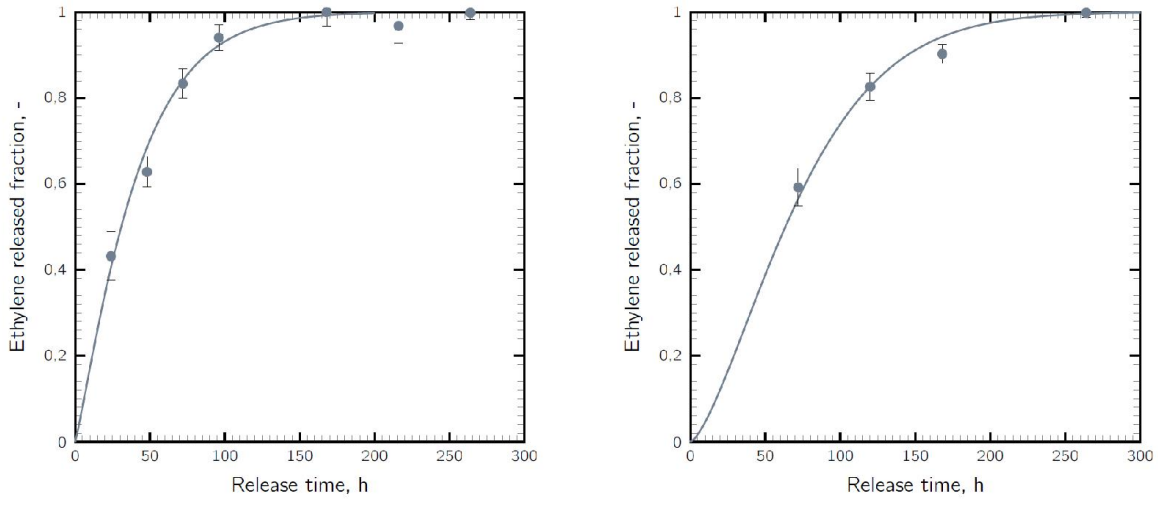


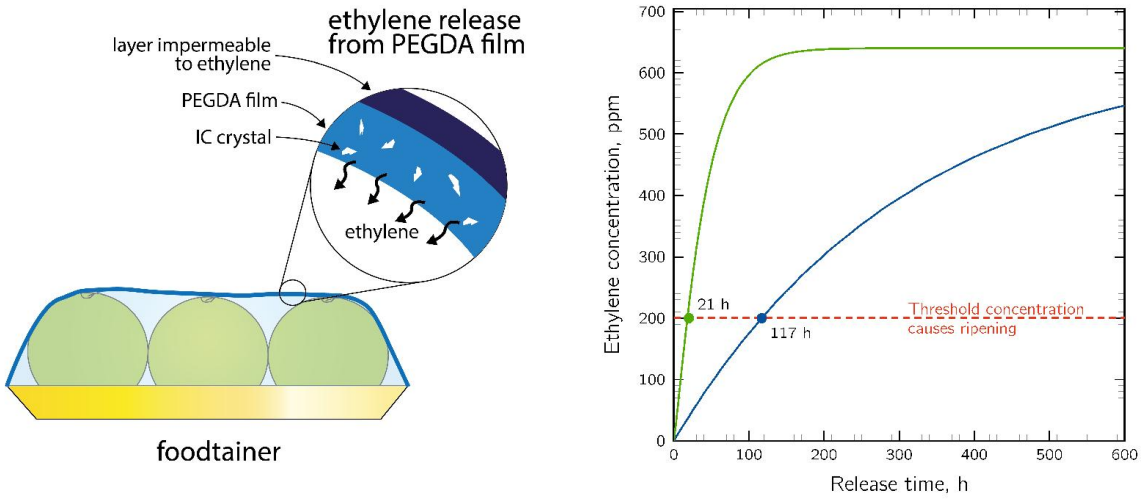
FIGURE 6. Release curves of ethylene from polymeric thin film of PEGDA 700 at 25°C (a) in an atmosphere saturated with water and (b) with a relative humidity of 97%.

The release curve showed a sharp slope at the beginning followed by a plateau. That behaviour seems to be well described with the Avrami equation[11,12]:

$$\varphi = 1 - e^{-\kappa t^{\theta}} \tag{1}$$

where φ is the molar fraction of ethylene released, κ is the release rate constant, θ is a parameter linked to the release mechanism and t is the release time. The value of κ depends on temperature and relative humidity, is product specific and its dependence on temperature is typically described by an Arrhenius-type equation. The solid lines of Fig.5 and Fig.6 represent the plot of Avrami equation with the value of κ and θ obtained from the best fit of the experimental data. In this work the values of θ were found to be about 1, while the values of κ were strongly affected by temperature and relative humidity.

The estimation of κ and θ can be useful in order to predict ethylene release in different conditions, and to control fruit ripening. Fig.7 shows a simulation of the time of ripening (estimated from the Avrami model) for typical fruit packaging (20.4×13.6×2.7cm) suited for 6 apples of approximately 6.8 cm diameter. Two different simulations are envisaged: the foodtainer is made of an ethylene-impermeable film and IC crystals (0.02g) are placed in the foodtainer, or the foodtainer is covered with a double-layer polymeric film, with the inner layer made of PEGDA filled with a certain quantity of IC (0.02 g) and the outer was an ethylene-impermeable film. The free total volume in the foodtainer is about 0.90 l and the value of ethylene concentration needed to start ripening is 200 ppm



(a) (b)

FIGURE 7. (a) Schematic of a foodtainer containing 6 apples and covered by a double-layer polymeric film which the internal layer made of PEGDA filled with IC and the external made of ethylene-impermeable polymer. (b) Ethylene concentration curve in the foodtainer in case of ICs (—) and PEGDA filled with ICs (—). Release curves were calculated by the Avrami equation with the following parameters: for ICs κ=0.00320 and θ=1.000; for PEGDA κ= 0.01356 and θ=1.148.

The ethylene concentration curves showed that in case of ICs the concentration threshold of 200 ppm was reached after 117 hours (more than 4 days), whereas in case of PEGDA film the time is reduced to only 21 hours.

CONCLUSIONS

In this work, inclusion complex of ethylene/α-cyclodextrin was produced by molecular encapsulation technique and used as a filler for UV-cured PEGDA films intended for fruit packaging.

PEGDA was found to be a good polymer matrix as its water affinity allows a quick and controlled ethylene release. Release rate from ICs results in slower dynamics than that observed in PEGDA filled films. It can be asserted that hydrophilic PEGDA matrix promotes the ethylene release by absorbing water vapor from the atmosphere and does not offer a relevant resistance to the gas diffusion.

This work might represent a basis for forward research in gases release from inclusion complex and smart food packaging.

The results show the great possibility of a precise control of concentration of ethylene in a ripening chambers in order to achieve a homogenous and complete ripening, and avoiding the worst phenomena of overriping.

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